Please note:

If you experience some difficulty in viewing some of the pages, use the magnifying tool to enlarge the specific section

UCRL- 92357
PREPRINT

The Microdetermination of Cyanide Complexes of Group VIIIA, IB, and IIB Elements

Walter S. Selig

This paper was prepared for submittal
to
Microchem, Journal

March 1985

Lawrence
Livermore
National
Laboratory

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

THE MICRODETERMINATION OF CYANIDE COMPLEXES OF GROUP VIIIA, IB, and IIB ELEMENTS

WALTER S. SELIG*

*Lawrence Livermore National Laboratory, University of California,
Livermore, CA 94550

Received

INTRODUCTION

We have previously used cetylpyridinium chloride (CPC) as the titrant for the precipitation titration of mercuric cyanide (12) and platinum(II)cyanide (13). Potassium aurocyanide, however, yielded very poor titration curves. Aurocyanide could be determined by titration with silver nitrate (14). In this paper we have explored both titrants for the determination of cyanide complexes of groups VIIIA, IB, and IIB.

EXPERIMENTAL

The indicating electrode for titrations with CPC was a spectrographic graphite rod coated with a solution of poly(vinylchloride) and dioctylphthalate in tetrahydrofuran, as previously described (9, 11). The indicating electrode for argentimetric titrations was an Orion 94-16A silver/sulfide ion-selective electrode (ISE). The reference electrode in both cases was a double-junction Ag/AgCl electrode (Orion No. 90-01) with a 0.1 M sodium nitrate salt bridge. The titration system was controlled by a Tektronix 4051 graphics computer system which has previously been described (7). Titration rates were kept constant at 0.3 ml/min. Stirring was provided by a magnetic stirrer. The stirring motor was isolated from the titration vessel by a water cooled plate and by a grounded aluminum plate. Titrations were performed at 23 ± 1°C. Titration endpoints were calculated by the second derivative method as previously described (7).

The titrants were 0.01 M aqueous solutions of CPC and silver nitrate. All other chemicals were of the highest purity available. The cyanide complexes used are listed in Table 1.

RESULTS AND DISCUSSION

We previously found that $KAu(CN)_2$, a compound important in gold plating solutions, could not be titrated with CPC, because very poor endpoint breaks were obtained. Titration with silver nitrate proved feasible, however, according to the equation

$$Au(CN)_2^- + Ag^+ \longrightarrow Ag[Au(CN)_2]\downarrow \qquad (1)$$

Indeed, this method seems to be general for cyanide complexes and has proved useful in our laboratory for the determination of some heavy metal cyanides (12, 13).

Titrimetric methods were found in the literature only for cyanoferrate (1, 4, 6), cyanocobaltate (4, 18), and pentacyanonitrosylferrate (17). Most of these methods use silver nitrate as titrant while mercuric nitrate has also been used (17).

For most of the cyanide complexes of groups VIIIA, IB, and IIB, both titrants were found suitable. The results are summarized in Table 1, which also gives the feasible pH ranges for both titrants. The stability constants of some metal cyanides are summarized in Table 2. Based on this information, however, no *a priori* conclusion is possible as to their stability in acid solutions. Moreover, wide variations were found in the literature in the values of the constants.

Most of the cyanides, with the exception of those of nickel, zinc, and mercury(II), were stable in acid solutions. Nevertheless, the nickel cyanide complex can be estimated with silver nitrate because it rapidly reacts to form AgCN according to

$$Ni(CN)_4^{2-} + 4\,Ag^+ \longrightarrow 4\,AgCN\downarrow + Ni^{2+} \qquad (2)$$

$Zn(CN)_4^{2-}$ and $Hg(CN)_4^{2-}$, however, react at a much slower rate and can be determined only by titration with CPC. The cyanide complexes which are unstable in acid solutions also are decomposed by formaldehyde which complexes cyanide according to

$$CN^- + HCHO \longrightarrow CNCH_2OH \qquad (3)$$

$Ag(CN)_2^-$ is also decomposed by formaldehyde. This compound (Table 1) can be titrated with silver nitrate only within a fairly narrow pH range, unlike the other compounds tested.

$Zn(CN)_4^{2-}$ and $Hg(CN)_4^{2-}$ (the two complexes that could not be determined by titration with silver nitrate) required an excess of cyanide for their successful titration with CPC. For the zinc complex the optimum was a 32-fold excess, while for the mercury complex it was from 60 to 120-fold. Apparently the excess cyanide stabilized the cyanide complex.

The recoveries in the titration of various cyanide complexes are shown in Table 3. A typical equation for the precipitation titration with CPC is shown for platinum cyanide:

$$Pt(CN)_4^{2-} + 2\ C_{21}H_{38}N^+ \longrightarrow (C_{21}H_{38}N)_2Pt(CN)_4\downarrow \qquad (4)$$

where $C_{21}H_{38}N^+$ is the cetylpyridinium cation. Simple cyanides may be converted to cyanide complexes by addition of excess cyanide according to

$$Pt(CN)_2 + 2\ CN^- \longrightarrow Pt(CN)_4^{2-} \qquad (5)$$

Some of the cetylpyridinium and silver salts were isolated by filtration, washing with water, and air-drying. Analytical data for the recovered materials are shown in Table 4. The existence of the hydrates of the cetylpyridinium salts of $Pd(CN)_4^{2-}$, $Pt(CN)_4^{2-}$, and $Ru(CN)_6^{4-}$ was confirmed by thermogravimetric analysis. Typical titration curves were presented elsewhere (12-14).

The initial emf of cyanide-free complex cyanides with the electrode pair used was near 50 mV. Free cyanide will lower this emf, the amount depending on the quantity of free cyanide (14). A mere 1 mg of free cyanide will lower the initial emf by as much as 500 mV. $Au(CN)_2^-$ and $Pt(CN)_4^{2-}$ can be estimated in the presence of free cyanide by adding formaldehyde until the pH is near 5-6 and letting the solution stand for 15 min before titration with silver nitrate. If an estimate of the amount of the free cyanide is required, the addition of formaldehyde is omitted. In this case titration with silver nitrate will yield 2 potentiometric breaks. The first break is due to the complexation of free cyanide (2) according to

$$Ag^+ + 2\ CN^- \longrightarrow Ag(CN)_2^- \qquad (6)$$

and the second break is due to the precipitation of the silver cyanide complex

$$Ag^+ + Ag(CN)_2^- \longrightarrow Ag[Ag(CN)_2] = 2\ AgCN\downarrow \qquad (7)$$

plus the precipitation of the gold or platinum cyanide complex according to Equation (1). If the volume at the first break is designated as "a", and the volume at the second break as "b" then

$$\text{volume of titrant for free cyanide} = a$$

$$\text{volume of titrant for complex cyanide} = b - 2a$$

Obviously, if large amounts of free cyanide are present the difference between "a" and "b" may be too large to handle conveniently. In this case complexation of the free cyanide with formaldehyde is recommended. For an estimate of the free cyanide a suitable smaller aliquot should be used.

When free cyanide is present, the results for the complex cyanide are less accurate than in its absence, probably because of coprecipitation of the two species.

If chloride is present, such as in the presence of $Au(CN)_2^-$, $Ag(CN)_2^-$, or $Os(CN)_6^{4-}$, both anions can be determined by sequential titration with silver nitrate. The first break is due to the complex cyanide while the second break is equivalent to the sum of chloride and the complex cyanide. This separation is feasible only when the solubility product of the complex cyanide is smaller than that of silver chloride. No separation was possible for chloride in the presence of cyanoferrate(II) or (III). Titration curves for aurocyanide in the presence of cyanide as well as chloride were previously presented (14).

The $K_2Pt(CN)_4 \cdot 3H_2O$ used contained some free cyanide, hence only an estimate was possible by silver nitrate titration. The presence of free cyanide, however, does not present a problem in the titration with CPC. In fact, as already mentioned, an excess of cyanide is required for optimum results with $Zn(CN)_4^{2-}$ and $Hg(CN)_4^{2-}$.

While additional complex cyanides, such as cyanochromate, cyanomanganate, and cyanocadmate were not available to us, they probably can also be determined by at least one of the methods presented above.

ACKNOWLEDGMENT

The writer thanks Glendon L. Crossman for the thermogravimetric analyses, and Randy E. Benson and Richard E. Whipple for the elemental analyses.

SUMMARY

Two titrimetric methods for the determination of complex cyanides of the elements of groups VIIIA, IB, and IIB are presented. The titrants are silver nitrate (using a silver/sulfide ion-selective indicating electrode) and cetylpyridinium chloride [using a poly(vinylchloride)/dioctylphthalate-coated graphite indicating electrode]. Silver nitrate can be used for all the complexes with the exception of $Zn(CN)_4^{2-}$ and $Hg(CN)_4^{2-}$, which react too slowly with silver. In many cases the sequential titration of free cyanide, complex cyanide, and free halide is feasible with silver nitrate, although the results are less accurate for the complex cyanide because of coprecipitation. Cetylpyridinium chloride can be used for all the complex cyanides tested with the exception of $Ag(CN)_2^-$ and $Au(CN)_2^-$. Halides and free cyanide do not interfere with determinations using this titrant.

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. 7405-ENG-48.

REFERENCES

1. Asplund, J., Titration of cyanide and hexacyanoferrate(II) with silver nitrate. Talanta 25, 143-146 (1978).
2. Conrad, F. J., Potentiometric titration of cyanide and chloride, using the silver specific-ion electrode as an indicator. Talanta 18, 952-955 (1971).
3. Högfeldt, E. (compiler), "Stability Constants of Metal-Ion Complexes," IUPAC Chemical Data Series No. 21. Pergamon, Oxford, 1982.
4. Krtil, J., Analysis of difficultly soluble hexacyanoferrates(II) and hexacyanocobaltates(III). Coll. Czech. Chem. Commun. 39, 4495-4500 (1967).
5. Nenadkevich, K. A., and Saltykova, V. S., Gravimetric and electrolytic methods for the separation and determination of nickel and cobalt in cyanide complexes. Zhur. Anal. Khim. 1, 123-128 (1946).
6. Saxena, R. S., and Bhatnagar, C. S., Potentiometric determination of potassium ferricyanide. Analyt. Chim. Acta 19, 402-405 (1958).
7. Selig, W., Potentiometric semimicrodetermination of some anions with 1,2,4,6-tetraphenylpyridinium acetate. Mikrochim. Acta II, 75-81 (1978).
8. Selig, W., Potentiometric microtitration of anions with cetyltrimethylammonium bromide. Mikrochim. Acta II, 373-381 (1979).
9. Selig, W., A simple sensor for potentiometric titrations. Anal. Letters 15(A3), 309-329 (1982).
10. Selig, W., Comparison of various sensors in the potentiometric microdetermination of nitroform and perchlorate with cetylpyridinium chloride. Mikrochim. Acta I, 333-345 (1983).

11. Selig, W. S., Potentiometric titrations using pencil and graphite sensors, J. Chem. Educ. 61, 80-81 (1984).

12. Selig, W. S., The potentiometric titration of mercury(II) with cetylpyridinium chloride. Mikrochim Acta II, 455-461 (1984).

13. Selig, W. S., Potentiometric titration of gold, platinum and some other precious metals with cetylpyridinium chloride. Fresenius' Z. Anal. Chem. (in press).

14. Selig, W. S., The potentiometric determination of gold in gold plating solutions by titration with silver nitrate. Plating Surf. Fin. (in press).

15. Sillen, L. G., and Martell, A. E. (compilers), "Stability Constants of Metal-Ion Complexes," Special Publication No. 17. The Chemical Society, London, 1964.

16. Sillen, L. G., and Martell, A. E. (compilers), "Stbility Constants of Metal-Ion Complexes Supplement No. 1," Special Publication No. 25. The Chemical Society, London, 1971.

17. Siska, E., and Pungor, E., Potentiometric titration of sodium pentacyanonitrosylferrate(III). Talanta 19, 715-716 (1972).

18. Uzel, R., and Jecek, B., Volumetric determination of the cobalticyanide ion. Coll. Czech. Chem. Commun. 7, 497-511 (1935).

TABLE 1

Compounds Used and Experimental Conditions

		Feasible pH range		
Ion determined	Compound used	Silver nitrate	Cetylpyridinium chloride	References
$Fe(CN)_6^{3-}$	$K_3Fe(CN)_6$	1 - 10.2	1.8 - 10	vs. CETAB (8)
$Fe(CN)_6^{4-}$	$K_4Fe(CN)_6 \cdot 3H_2O$	0.8 - 10.2	1 - 11.3	vs. CETAB (8)
$Fe(CN)_5(NO)^{2-}$	$Na_2Fe(CN)_5(NO) \cdot 2H_2O$	0.7 - 10	1 - 11.5	vs. CPC (9)
$Co(CN)_6^{3-}$	$K_3Co(CN)_6$	1 - 10	1.9 - 11.2	
$Ni(CN)_4^{2-}$	$K_2Ni(CN)_4$	dec. to AgCN[a]	≥ 6.7 - 10.9	
$Zn(CN)_4^{2-}$	$K_2Zn(CN)_4$	dec. to AgCN[b]	≥ 9 (excess cyanide required)	
$Ru(CN)_6^{4-}$	$K_4Ru(CN)_6 \cdot 3H_2O$	1.2 - 6	≥ 4	
$Pd(CN)_4^{2-}$	$K_2Pd(CN)_4 \cdot 3H_2O$	1.2 - 10	2 - 11	
$Ag(CN)_2^-$	$KAg(CN)_2$	5.4 - 6.7	not feasible	
$Os(CN)_6^{4-}$	$K_2Os(CN)_6 \cdot 3H_2O$	1.8 - 7.4	3.9 - 11.2	
$Ir(CN)_6^{3-}$	$Na_2Ir(CN)_6$ Solution	not feasible	2 - 6.7	
$Pt(CN)_4^{2-}$	$K_2Pt(CN)_4 \cdot 3H_2O$	0.9 - 9.5	1.1 - 11.0	
$Pt(CN)_6^{2-}$	$K_2Pt(CN)_6$	1.2 - 11	2 - 10.4	
$Au(CN)_2^-$	$KAu(CN)_2$	1.2 - 6.6	very poor break	
$Hg(CN)_4^{2-}$	$K_2Hg(CN)_4$	dec. to AgCN[b]	9.6 (excess cyanide required)	

[a] reacts rapidly

[b] reacts slowly hence no analytically useful results were obtained

TABLE 2

Stability Constants of Metal Cyanide Complexes (3, 13, 14)

Complex	log β_n	Temp. °C
$Fe(CN)_6^{3-}$	31 - 43.9	25
$Fe(CN)_6^{4-}$	24 - 36.9	25
$Co(CN)_6^{3-}$	64	2
$Ni(CN)_4^{2-}$	11.7 - 31	25
$Zn(CN)_4^{2-}$	16.8 - 19.6	25
$Pd(CN)_4^{2-}$	42.4 - 51.6	0
$Ag(CN)_2^{-}$	18.4 - 20.9	25
$Pt(CN)_4^{2-}$	41	18
$Au(CN)_2^{-}$	36.6 - 38.3	25
$Hg(CN)_4^{2-}$	40.4 - 43.5	25

TABLE 3

Statistics for the Recovery in the Analysis of Some Cyanides

Anion	Taken, mg	Recovered, mg ± 95% limits	Number of replicates	titrant
$Fe(CN)_6^{3-}$	2.698	2.710 ± 0.013	7	$AgNO_3$[a]
$Fe(CN)_6^{4-}$	2.563	2.562 ± 0.002	6	$AgNO_3$[a]
$Fe(CN)_5(NO)^{2-}$	7.395	7.396 ± 0.010	6	$AgNO_3$
	2.922	2.920 ∓ 0.008	7	CPC
$Co(CN)_6^{3-}$	2.865	2.780 ± 0.009	6	$AgNO_3$
	2.865	2.860 ∓ 0.006	6	CPC
$Ni(CN)_4^{2-}$	2.953	2.849 ± 0.011	6	$AgNO_3$[b]
	2.953	2.955 ∓ 0.006	7	CPC
$Zn(CN)_4^{2-}$	3.030	3.029 ± 0.021	6	CPC
$Ru(CN)_6^{4-}$	2.938	2.936 ± 0.011	6	$AgNO_3$
	2.938	2.935 ∓ 0.003	6	CPC
$Pd(CN)_4^{2-}$	4.225	4.223 ± 0.010	7	$AgNO_3$
	4.225	4.224 ∓ 0.009	6	CPC
$Ag(CN)_2^-$	4.895	4.735 - 0.026	6	$AgNO_3$
$Os(CN)_6^{4-}$	3.448	3.451 ± 0.016	6	$AgNO_3$
	3.448	3.446 ∓ 0.012	6	CPC
$Ir(CN)_6^{3-}$	unknown	4.89 ± 0.06	4	CPC
$Pt(CN)_4^{2-}$	5.320	5.318 ± 0.015	7	CPC
$Pt(CN)_6^{2-}$	5.345	5.342 ± 0.007	10	$AgNO_3$
	5.345	5.343 ∓ 0.015	6	CPC
$Au(CN)_2^-$	14.850	14.854 ± 0.010	6	$AgNO_3$
$Hg(CN)_4^{2-}$	4.790	4.786 ± 0.046	4	CPC

[a] see Reference 8 for titration vs cetyltrimethylammonium bromide

[b] equivalent weight equals 1/4 of molecular weight because of decomposition to AgCN

TABLE 4

Elemental Analyses of Some Recovered Precipitates

Compound	Calculated, percent			Found, percent		
	C	H	N	C	H	N
$(C_{21}H_{38}N)_2Fe(CN)_5(NO)$	68.42	9.29	13.58	68.37	9.30	13.28
$Ag_3[Co(CN)_6]$	13.38		15.60	13.71	0.16	15.45
$(C_{21}H_{38}N)_3Co(CN)_6 \cdot 2H_2O$	71.16	10.21	10.82	71.06	9.80	10.88
$(C_{21}H_{38}N)_2Ni(CN)_4$	71.58	9.92	10.89	71.48	9.94	10.25
$(C_{21}H_{38}N)_2Zn(CN)_4 \cdot 2H_2O$	67.82	9.90	10.32	67.45	9.36	10.25
$Ag_4[Ru(CN)_6]$	10.46		12.20	11.05		12.12
$(C_{21}H_{38}N)_4Ru(CN)_6 \cdot 4H_2O$	69.86	10.42	9.05	69.17	10.26	9.07
$Ag_2[Pd(CN)_4]$	11.29		13.16	11.33		12.62
$(C_{21}H_{38}N)_2Pd(CN)_4 \cdot 2H_2O$	66.46	8.92	9.30	66.05	9.19	9.41
$(C_{21}H_{38}N)_3Ir(CN)_6 \cdot 2H_2O$	63.85	9.16	9.71	64.10	9.25	9.41
$Ag_2[Pt(CN)_4]$	9.33		10.88	9.79	0.11	10.27
$Ag_2[Pt(CN)_6]$	12.72		14.84	13.30		14.33
$(C_{21}H_{38}N)_2Pt(CN)_4 \cdot H_2O$	59.64	8.49	9.07	59.74	8.35	8.54
$Ag[Au(CN)_2]$	6.73		7.85	7.03		7.71
$(C_{21}H_{38}N)Au(CN)_2$	49.91	6.92	7.59	49.89	6.90	7.25
$Ag_2[Hg(CN)_4]$	9.23		10.77	9.91		10.18
$(C_{21}H_{38}N)_2Hg(CN)_4$	60.47	8.38	9.20	59.60	8.21	9.06